

THE ADDITION OF THE GRIGNARD REAGENT TO MESITONAPHTHONES

BY

FRED WALTER SPANGLER

A.B., Carthage College, 1940

M.S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

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INTRODUCTION

The Grignard reagent reacts normally with ketones having unhindered carbonyl groups to give carbinols.¹ When highly hindered ketones were investigated initially it was generally assumed that the carbonyl group in aryl mesityl ketones would not be attacked by Grignard reagents. It has been shown, however, that reactions of aryl mesityl ketones with Grignard reagents do take place, the course of the reaction and the products formed being determined by the structures of the initial ketone and of the Grignard reagent. Benzoylmesitylene was found to react with methylmagnesium iodide to give 1-mesityl-1-phenylethylene, the dehydration product of the carbinol that would have resulted from 1,2 addition.² *p*-Toluylmesitylene³ and benzoylisodurene⁴ were found to react in a similar manner. Aryl Grignard reagents have been shown to react with aryl mesityl ketones in the 1,4 manner involving a double bond of the aryl group.⁵ The present investigation was undertaken for the purpose of studying the reaction of the Grignard reagent with mesitonaphthones.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Methylmagnesium iodide has been found to add to 1-mesitonaphthone in the 1,4 manner involving a double bond of the naphthalene nucleus. Hydrolysis of the enolate gave an enol which readily ketonized to form 1,2-dihydro-2-methyl-1-mesitonaphthone (I), m.p. 86°. The addition compound I was converted into an acetate (II), m.p. 115°, by treatment with acetic anhydride and pyridine. Oxidation of I with chromic anhydride yielded a substituted naphthoquinone (III), m.p. 195-196°. Treatment with bromine in carbon tetrachloride converted I into a dibromide (IV), m.p. 162-163° (decomp.). The addition compound I was shown to be different from 1-mesityl-1-(1-naphthyl)ethylene (V), m.p. 98-99°, which was obtained from the reaction of mesitylmagnesium bromide with 1-acetonaphthone. The structure of I was established by dehydrogenation with palladium-charcoal catalyst to give the known 2-methyl-1-mesitonaphthone.⁶ The structure of I was fur-

ther substantiated by identification of the cleavage products of the peroxide prepared from the enol intermediate. Mesitoic acid and 4,4'-dihydroxy-3,3'-dimethyl-1,1'-dinaphthyl⁷ were isolated and identified.

The reaction of methylmagnesium iodide with 2-mesitonaphthone appears to be more complex. The first step presumably involves 1,4 addition of the Grignard reagent. When the Grignard addition complex was decomposed in the presence of air, compound VI, m.p. 98.5-100°, was obtained, the properties of which are in agreement with those to be expected for the aromatic ketone that would have resulted from 1,4 addition followed by oxidation involving the loss of a molecule of hydrogen or its equivalent. Compound VII, m.p. 209-210°, was also obtained. Its properties indicated that it was probably a bimolecular product, such as a pinacol. When VII was recrystallized from glacial acetic acid containing a small crystal of iodine, it was converted into compound VIII, m.p. 316-318°. Decomposition of the Grignard addition complex in an atmosphere of nitrogen produced compound IX, m.p. 73-74°, the properties of which are in agreement with those to be expected for the hydroaromatic ketone that would have resulted from 1,4 addition of the Grignard reagent followed by ketonization of the enol intermediate. Compound IX was converted into compound VI by dehydrogenation with palladium-charcoal catalyst. Oxidation of the enol intermediate obtained by decomposition of the Grignard addition complex produced a crystalline peroxide (X), m.p. 172-174°, which decomposed rapidly when heated slightly above the melting point.

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VITA

The author was born in Park Ridge, Illinois, on February 27, 1918. He attended the public schools of that city and was graduated from Maine Township High School in June, 1936. He entered Carthage College in the fall of 1936 and received the degree of Bachelor of Arts in June, 1940. In the fall of 1940 he entered the Graduate School of the University of Illinois and received the degree of Master of Science in February, 1942. He held a teaching assistantship from 1940 to 1942 and a University Fellowship from 1942 to 1944.



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